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DEGRADATION OF MONOCHLOROACETIC ACID BY ALUMINIUM MODIFIED FENTON PROCESS

Memòria i Annexos

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Resum

Aquest projecte investiga la degradació de l'àcid monocloroacètic (MCA) a partir d'una modificació del procés Fenton amb alumini. S'ha estudiat la reacció Fenton I s'ha modificat amb alumini sòlid (ZVAl) i ions Al^{3+}. Els factors estudiats que poden influenciar la reacció són les quantitats de peròxid d'hidrogen, ZVAl I Al^{3+}. A més a més, la influència dels agents quelants com l'àcid oxàlic i l'àcid cítric també s'ha estudiat. En tots els sistemes s'ha aconseguit degradar l'MCA I la reacció Fenton s'ha aconseguit millorar. L'àcid cítric sembla la millor opció per millorar la reacció de Fenton clàssica. La toxicitat de la degradació de l'MCA s'ha estudiat per diferents eficiències. Pels resultats obtinguts és evident que la modificació de la reacció Fenton és una alternativa a considerar per degradar contaminants clorats amb alta concentració.

Paraules clau: ions d'alumini, reacció Fenton , agents quelants , àcid monocloroacètic, test de toxicitat,

Resumen

Este proyecto investiga la degradación del ácido monocloroacético (MCA) a partir de una modificación del proceso Fenton con aluminio. La reacción Fenton y su modificación con aluminio solido (ZVAl) y iones de aluminio Al^{3+} se ha estudiado. Se han considerado como factores influyentes en la reacción las cantidades de peróxido de hidrogeno, ZVAl y Al^{3+}. Además, la influencia de los agentes quelantes como el ácido oxálico y el ácido cítrico también se ha estudiado. En todos los sistemas se ha conseguido degradar el MCA y la reacción Fenton se ha mejorado. El ácido cítrico parece una mayor alternativa para mejorar la reacción clásica de Fenton. La toxicidad de la degradación del MCA resultante del tratamiento se ha estudiado para distintas eficiencias. Con los resultados obtenidos, parece evidente que esta modificación del Fenton es una buena alternativa para degradar contaminantes clorados con alta concentración.

Palabras clave: iones de aluminio, reacción Fenton , agentes quelantes , ácido monocloroacético, test de toxicidad,

Abstract

This study investigates the degradation of monochloroacetic acid (MCA) by aluminium modified Fenton Process. Fenton reaction and its modifications using zero-valent aluminium (ZVAl) and Al^{3+} ions have been performed. Influencing factors such as different amounts of hydrogen peroxide, ZVAl and aluminium ions have been studied. Also, the influence of chelating agents (oxalic and citric acids) has been studied. In each system MCA degradation has been achieved and classical Fenton reaction has been improved. Citric acid seems to be a better option to improve the efficiency of the classical Fenton reaction. Environmental toxicity of some resulting solutions with the best efficiencies of degradation has been investigated. From obtained results it is clear, that aluminium modified Fenton reaction is promising method for the degradation of chlorinated pollutants in high concentration.

Keywords: Aluminium ions, AOPs, Fenton reaction, Chelating agents, Monochloroacetic acid, Toxicity tests, Zero-valent aluminium.

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List of abbreviations

AOPs	Advanced Oxidation Processes
CAA	chelating agents
CA	Citric acid
CMC	Carboxymethyl-cellulose
COD	Chemical Oxygen Demand
E°	redox potential
FR	Fenton reaction
HAA	Haloacetic acids
MCA	Monochloroacetic acid
OA	Oxalic acid
PEC	Predicted Environmental Concentration
ROS	Reactive Oxygen Species
US	ultrasound
UV	ultraviolet
ZVAl	Zero-valent aluminium
ZVI	Zero-valent iron

Content

1. Introduction

Due to industrialization, the generation of wastewater is continuously growing up and this is an environmental problem that must be taken into account. Contaminated soil, agricultural runoff, industrial wastewater and hazardous compounds leakage are example of sources that produce ground water and surface water contamination. Lots of industrial activities and above all the chemical one, produce wastewaters with a diversity of toxic, non-biodegradable and persistent organic pollutants. These organic compounds are an important issue for public health because of their toxic, mutagenic and potentially carcinogenic properties even in low concentrations.

For this reason, the need to treat those streams is essential but this is not an easy challenge due to the confluence of different priorities. From an economical point of view wastewater should be treated as inexpensively as possible. However, some regulations must be met by the effluent discharge and the treatment should be environmentally friendly and if it is possible operated on-site. In addition, reuse and recycling options must not be forgotten.

Microbial degradation is one of the most used wastewater treatment processes (Wang et al., 2014). However, while most of the easily biodegradables compounds can be eliminated with this treatment, some recalcitrant compounds persist in the streams and end in the environment. At this point is when Advanced Oxidation Processes (AOPs) seems a promising alternative to treat this compound and in recent years lots of investigations have been conducted (Bautista et al., 2008).

Basically, AOPs are able to oxidize organic compounds mostly by hydroxyl radical ($HO^{\bullet}$) and if it need mineralized them into CO_2 and water. These processes can be classified as chemical or photochemical AOPs processes. Further information is presented in section 2.2.

In this project, monochloroacetic acid (MCA) as a model priority pollutant is degraded by different AOPs processes which are able to produce $HO^{\bullet}$ radicals. The aim is to achieve the maximum degradation efficiency. Environmental toxicity of some resulting solutions has been investigated.

1.1. Main goals

The main goal of this Project is to study the degradation of MCA by aluminium modified Fenton process and try to find out the best operation conditions. Also, it is important to know how the influencing factors studied can affect the degradation rate.

Finally, the aim of this Project is to know the toxicity of the treated solutions in order to see its environmental impact.

1.2. Scope

The scope of this research is to study the degradation of MCA and improve the classical Fenton reaction. The mechanism of the degradation it is not investigated. There are a lot of influencing factors that can affect the reaction but only those ones specified are performed.

It is not the scope of this project to offer an industrial application of the classical Fenton modification. This is a research to improve Fenton reaction but its application to industrial scale should be studied better.

2. Theoretical part

In order to have a widely view of the whole project and understand better the results some information about monochloroacetic acid (MCA) and its environmental relationship is provided. Also, AOPs are generally described, and a deep explanation about performed reactions and studied influencing factors are presented.

2.1. Occurrence of monochloroacetic acid in environment

In the last years, haloacetic acids (HAAs) have been loaded into the environment, as they are present in wastewater because of some human activities, causing environmental problems (Loos et al., 2001). Monochloroacetic acid is the most occurring HAAs. Because of using chlorine for drinking water disinfection, MCA has been detected around the world in drinking water in trace amounts (Ghassempour et al., 2006). This pollutant has been found in rainwater, surface waters, soil and snow (Beschkov et al., 2005) due to its production also by different biological processes. The Predicted Environmental Concentration in water (PEC) for MCA is about 0.58 $\mu g \cdot l^{-1}$ (IHCP, 2005).

MCA is a colorless crystalline substance and as it is shown in table 1, it has a low vapor pressure and high water solubility. For this reason MCA can be expected in wastewater streams and subsequently in water ecosystem as water pollutant.

MCA is produced by chlorination of acetic acid or hydrolysis of trichloroethylene using sulfuric acid (NAP, 2009). It is used as a reagent for the synthesis of other products such as carboxymethyl-cellulose (CMC), crop protection chemicals, cosmetics, flavors, plastics and other organic compounds. It is classified as priority pollutant in environment because of its phytotoxic and carcinogenic effect. As MCA is an acid (pK_a = 2.85), it can cause irritation of the eyes and skin with direct contact in skin even in small concentrations. Its toxic effect is produced by the inhibition of enzymes of the glycolytic pathway and the tricarboxylic acid cycle (NAP, 2009). This metabolic failure damages organs such as heart, central nervous system, and muscles because of their high-energetic need.

Table 1 - Physico-chemical properties of MCA (RIVM, 2008)

Parameter	Unit	Value	Remark
Molecular weight	[g mol^{-1}]	94.5	
Water Solubility	[g L^{-1}]	4.210	at 20ºC
pK_a	[-]	2.85	at 25ºC
Vapor pressure	[Pa]	<100	at 20ºC
		8.7	at 25ºC
		1100	at 80ºC
Melting point	[ºC]	61.5-62.3	
Boiling point	[ºC]	189	at 101.3 kPa
Henry's law constant	[Pa m^3 mol^{-1}]	1.9 10^{-4}	at 20ºC

At the present, many natural and anthropogenic sources of halogenated compounds are known. One of them is degradation process of chlorinated compounds such as 1,1,1-trichloroethane and trichloroethene in atmosphere (Ballschmiter, 2003). MCA is formed also in soil by biological chlorination of humic acids in the presence of chloride ions, hydrogen peroxide and enzyme chloroperoxidase (Fahimi et al., 2002). Different MCA concentration values for some environmental ecosystems are presented in table 2.

As MCA is a priority pollutant, many studies have been focused on its degradation. Different techniques have been tested like electrolysis (Yang et al., 2014), sulfite/UV process (Fang et al., 2012) or biodegradation (Beschkov et al., 2005). The aim of this project is to study the MCA degradation using Fenton and modified Fenton process as an $HO^{\bullet}$ generation methods.

Table 2 – Environmental risk limits for MCA

	Unit	MPC [(a)]	NC [(b)]	MAC_{eco} [(c)]	SRC_{eco} [(d)]
Water	[$\mu g\ L^{-1}$]	0.58	5.8×10^{-3}	0.58	9600
Drinking water	[$\mu g\ L^{-1}$]	0.10			
Marine	[$\mu g\ L^{-1}$]	0.058	5.8×10^{-4}	0.058	9600
Soil	[$\mu g\ kg^{-1}$]	4.6	0.046		1800
Groundwater	[$\mu g\ L^{-1}$]	0.10	0.001		9600

(a) Maximum permissible concentration; (b) Negligible concentration; (c) Maximum acceptable concentration for ecosystems; (d) Serious risk concentration for ecosystems

2.2. Advanced Oxidation Processes for water treatment

As it has been said, biological treatment is not able to degrade all organic compounds because some of them are non-biodegradable or toxic for microorganisms. Therefore, oxidation processes are desired to treat these recalcitrant compounds. Although, direct oxidation processes are used to treat these biorefractory substances, their extreme operational conditions (175 - 325ºC) and its complicated free radical mechanisms, that may lead in even more toxic products (Prousek, 1996), make AOPs a better option to treat these compounds.

AOPs have been defined (Glaze *et al.,* 1987) as those processes that imply an $HO^{\bullet}$ generation in an enough amount to degrade the organic compounds that are in the wastewater. The last aim of these processes is the oxidation of pollutants in water in order to mineralize them, which is to convert these compounds into simple, harmless and inorganic molecules. AOPs are capable of converting the organic contaminant completely to CO_2 and water, if desired (Prousek, 1996).

The electronegative elements in the top right corner of the periodic table form the stronger oxidants (F, Cl, O, Br, S). The oxidation potential or the relative strength of the typical oxidants is shown in table 3. $HO^{\bullet}$ is a very reactive radical particle with high redox potential ($E^{\circ} = 2.80$ V), which is much higher than other oxidizing species like ozone ($E^{\circ} = 2.07$ V) or hydrogen peroxide ($E^{\circ} = 1.77$ V), (Parsons, 2004). That's the main reason why it is used to oxidation processes.

Table 3 – Standard reduction potential for common oxidants (Parsons, 2004)

Oxidant	Oxidation Potential (V)
Fluorine (F_2)	3.03
Hydroxyl radical ($HO^{\bullet}$)	2.80
Atomic oxygen (O)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Potassium permanganate ($KMnO_4$)	1.67
Chlorine dioxide (ClO_2)	1.50
Hypochlorous acid (HClO)	1.49
Chlorine (Cl_2)	1.36
Oxygen (O_2)	1.23
Bromine (Br_2)	1.09

As the $HO^{\bullet}$ is the most powerful oxidizing agent after fluorine, the main goal of all the AOPs is to produce $HO^{\bullet}$ in water. For instance, $HO^{\bullet}$ is able to oxidize some different organic compounds significantly faster than ozone as shown in table 4. Although $HO^{\bullet}$ is the most used oxidizing agent, it is part of the reactive oxygen species (ROS), which are chemically reactive molecules containing oxygen such as $HO^{\bullet}$, singlet oxygen ($^1O_2$), superoxide anion radical ($O_2^{\bullet -}$) and H_2O_2 (Cheng et al., 2015).

Once a free radical reaction is initiated by hydrogen peroxide, ozone, photolysis etc., then a lot of simple reactions will follow. The large number of subsequent reactions makes these systems very difficult to understand the mechanism of the oxidation and predict the oxidation products as well.

One advantage of the AOPs is the fact that they offer different possible ways for $HO^{\bullet}$ production, in a near ambient temperature and pressure, thus allowing a better compliance with the specific treatment requirements (Babuponnusami & Muthukumar, 2013). Moreover, because of $HO^{\bullet}$ reactivity, it reacts with almost every pollutant making them a good choice when many different pollutants are present in wastewater. Another advantage is that disinfection can also be achieved in AOPs making them an integrated solution for wastewater treatments (NWRI, 2000).

Table 4 – Second order rate constants for ozone and hydroxyl radical (Neyens, 2003; Hoigné, 1983)

Organic compound	**Rate constant ($M^{-1} s^{-1}$)**	
	O_3	$HO^{\bullet}$
Benzene	2	7.8×10^9
Toluene	14	7.8×10^9
Chlorobenzene	0.75	4×10^9
Trichloroethylene	17	4×10^9
Tetrachloroethylene	<0.1	1.7×10^9
n-Butanol	0.6	4.6×10^9
t-Butanol	0.03	0.4×10^9

However, AOPs have some limitations to be applied in an industrial scale due to its operational costs. Above all, the energetic consumption and the reagents cost such as oxidant reagents and catalyst (Rubio-Clemente et al., 2014). Besides this, alkalinity, nitrites and other inorganic compounds can limit the effectiveness of the process because of their scavenging of $HO^{\bullet}$. As a result, some pre-treatment might be needed (NWRI, 2000).

As it is shown in table 5, AOPs can be classified according to $HO^{\bullet}$ generation methods (chemical, electro-chemical, sono-chemical and photochemical) or according to the used phase (homogenous or heterogeneous). Very often a combination of all these methods is also used. Chemical method to produce $HO^{\bullet}$ will be deeply explained in the following sections due to it is the base of this project. A briefly description of the most important $HO^{\bullet}$ generation methods is provided.

The electro-chemical method is based in the direct/indirect anodic reactions and $HO^{\bullet}$ is formed on the electrode surface. On the other hand, in the sono-chemical process high frequency sound waves are used to generate transient or stable acoustic cavitation in water solution. The cavitation involves formation, growth and collapse of pressure bubbles with inducing thermal dissociation of water into hydroxyl radicals (Bokare & Choi, 2014).

In the photochemical method, aqueous solution is irradiated with UV photons and the species present in water then absorb the incident UV light and undergo photo-transformation reactions to generate free hydroxyl radicals (Babuponnusami & Muthukumar, 2013).

It is also important to highlight the ozonation process. This processes use a high voltage alternating current to dissociate O_2 into oxygen atoms to form ozone (O_3). Then, ozone gas stream is introduced in water and it decomposes to free $HO^{\bullet}$.

There are other non-conventional AOPs such as ionizing radiation, microwaves and pulsed plasma techniques but it is not the aim of this project to explain it.

Table 5 - Classification of conventional AOPs (Babuponnusami & Muthukumar, 2013)

Type of process	Example
Homogeneous	**Fenton based process**
	Fenton: $H_2O_2 + Fe^{2+}$
	Fenton like: $H_2O_2 + Fe^{3+}/M^{n+}$
	Sono-Fenton: US/ $H_2O_2 + Fe^{2+}$
	Photo-Fenton: UV/ $H_2O_2 + Fe^{2+}$
	Electro-Fenton
	Sono-electro-Fenton
	Photo-electro-Fenton
	Sono-photo-Fenton
	O_3 based processes
	O_3
	O_3 + UV
	$O_3 + H_2O_2$
	O_3 + UV + H_2O_2
Heterogeneous	$H_2O_2 + Fe^{2+}/Fe^{3+}/M^{n+}$ - solid
	TiO_2/ZnO/CdS + UV
	$H_2O_2 + Fe^{0}$/Fe (nano-zero valent iron)
	H_2O_2 + immobilized nano-zero valent iron

2.3. Fenton reaction

Among all AOPs, probably, the Fenton process using hydrogen peroxide and ferrous salts is one of the most used. Its effectiveness for the degradation of a wide range of pollutants has been proved and it has been applied to a number of different wastewater treatment processes (Bautista et al., 2008)

Fenton reaction was firstly postulated by H.J.H Fenton in 1894 and marked a new era in chemistry. It was found by accident that iron ions mixed with oxidizing agents could produce a solution with high oxidation capacities (Pulgarin et al., 2016).

Fenton reaction (FR) is based on the decomposition of hydrogen peroxide (H_2O_2) by ferrous ions (Fe^{2+}) to produce $HO^{\bullet}$ radicals, hydroxide anions (HO^-) and ferric ions (Fe^{3+}) under acidic conditions (Eq. 1). Moreover, with addition of higher amount of H_2O_2 it is possible to regenerate the Fe^{2+} ions (Eq. 2). This reaction is referred as Fenton-like (Neyens et al., 2002). Although these reactions are used to describe the process, the mechanism is much more complicated because of many other side reactions are also implied (Eq. 3-13). As shown in table 6, all participated reactions are classified into three groups: initiation, propagation and termination.

From all the implied equations in the mechanism, it is important to highlight that $HO^{\bullet}$ can be scavenged by hydrogen peroxide (Eq. 3), ferrous ions (Eq. 9), hydroperoxyl radicals (Eq. 12) or even scavenged by themselves (Eq. 13). Finally, if there are no organic molecules to be oxidized, hydrogen peroxide decomposes to oxygen and water (Eq. 14). This is an undesirable reaction due to the oxidant waste and it may lead to a surcharge.

Hence, when Fenton process is used to mineralize organic compounds, the main objective is to use initiation and propagation reactions and try to avoid undesirable termination reactions in which radicals react with iron or among them instead of oxidize organic compounds.

The advantages of the Fenton process, if it is compared to other oxidation AOPs processes, are that can be carried out in mild operating conditions without using complicated equipment. In addition, hydrogen peroxide is safe and easy to handle and it is environmentally-friendly. Due to the rapid reaction between iron and H_2O_2, the activation H_2O_2 and the generation of $HO^{\bullet}$ is done in the shortest time among all the AOPs (Babuponnusami & Muthukumar, 2013), and the high efficiency of mineralization let the transformations of organic pollutants into CO_2.

Table 6 – Reactions involved in Fenton process (Muñoz et al, 2015; Pignatello, 2006)

	Eq.	Reaction	Rate constant ($M^{-1} s^{-1}$)
Initiation	1	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet$	55
	2	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet$	2.00×10^{-3}
Propagation	3	$H_2O_2 + HO^\bullet \rightarrow H_2O + HOO^\bullet$	3.30×10^{7}
	4	$R{-}H + HO^\bullet \rightarrow R^\bullet + H_2O$	
	5	$R^\bullet + Fe^{2+} \rightarrow R^- + Fe^{3+}$	
	6	$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+}$	
Termination	7	$R^\bullet + R^\bullet \rightarrow R{-}R$	
	8	$Fe^{3+} + HOO^\bullet \rightarrow Fe^{2+} + O_2 + H^+$	7.82×10^{5}
	9	$Fe^{2+} + HO^\bullet \rightarrow HO^- + Fe^{3+}$	3.20×10^{8}
	10	$Fe^{2+} + HOO^\bullet \rightarrow Fe^{3++} + H_2O_2$	1.34×10^{6}
	11	$HOO^\bullet + HOO^\bullet \rightarrow H_2O_2 + O_2$	2.33×10^{6}
	12	$HOO^\bullet + HO^\bullet \rightarrow H_2O + O_2$	7.15×10^{9}
	13	$HO^\bullet + HO^\bullet \rightarrow H_2O_2$	5.20×10^{9}
	14	$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$	

Despite a lot of investigation is being carried out to find new viable catalyst, iron still remains the only choice as a metal catalyst to decompose H_2O_2 into $HO^\bullet$ (Bokare & Choi, 2014). There are some reasons that explain why iron is still the best option: it is very abundant on Earth, it has low toxicity, it is environmentally compatible and it has low commercial cost.

However, there is an important drawback when iron is used as a catalyst. Iron species (Fe^{2+}, Fe^{3+} and ferric hydroxides) have a strong dependence on the pH, so not for all the Fenton-based AOPs will have the same requirements. For instance, in classical Fenton reaction it is necessary to have Fe^{2+} or Fe^{3+} in the solution in order to get the highest efficiency. There is no problem with Fe^{2+} due to it remain in dissolved form even at neutral pH, but Fe^{3+} at pH ≥ 4 disappear to form ferric hydroxide

sludge. Hence, acidic conditions are needed to perform classical Fenton reaction and this lead into a high cost of chemicals needed for acidifying effluents before treatment. At the end of the process, the Fenton effluent is neutralized with sodium hydroxide or by lime and this implies the generation of iron sludge and the continuous loss of iron ions.

2.4. ZVI, nZVI and nano-magnetite in Fenton process.

Despite the fact that ZVI, nZVI and nano-magnetite are not part of the project, it is important to explain briefly each of them for different reasons. ZVI has been extensively applied for the treatment of groundwater and wastewater contaminated with various organic and inorganic pollutants in the last 20 years (Fu et al., 2013). Nano-magnetite and nZVI have recently gained much more attention because of its potential to enhance the pollutants removal.

As it has been said, iron is still the best catalyst choice. ZVI has been successfully applied for the Cr^{6+} removal (Fu et al., 2013). The removal mechanism of contaminants used by ZVI is the directional transfer of electrons from ZVI to the pollutants which are transformed in less toxic species. On the other hand, organic compounds can also be degraded by ZVI if dissolved oxygen is present in water. The reason is that ZVI transfers two electrons to O_2 to produce H_2O_2 (Eq. 15). Then, Fe^{2+} ions can be produced when ZVI gives again two electrons to H_2O_2 (Eq. 16). Finally, $HO^{\bullet}$ can be generated by Fenton reaction (Eq. 1).

$$Fe^0 + O_2 + 2\ H^+ \rightarrow Fe^{2+} + H_2O_2 \qquad (15)$$

$$Fe^0 + H_2O_2 + 2\ H^+ \rightarrow Fe^{2+} + 2\ H_2O \qquad (16)$$

Recently, nano-scale ZVI (nZVI) has gained interest and it has been widely applied to the remediation of contaminated soil and groundwater, as well as wastewater treatment. The reason is that nZVI particles are more reactive than micro-scale ZVI due to its extremely small particle size, large surface area, and mobility (Moon et al., 2011).

The nZVI-Fenton process combines the advantages of nZVI reduction and Fenton oxidation, and it is regarded as a very effective process for treating wastewater that contains dyes and other waste products from the textile manufacturing industry. In addition, the nZVI Fenton process is regarded as a greener process than the conventional Fenton process (Zha et al., 2014).

The nZVI-Fenton process also can reduce the typical problems associated with the conventional Fenton process, such as the consumption of significant quantities of chemical reagents and the production of significant quantities of chemical sludge, both of which increase operational costs. However, as the nZVI-Fenton process is much more complex and dynamic than the conventional

Fenton process, on-line monitoring and control are very critical for the optimal operation of the process (Yu et al., 2014).

Heterogeneous Fenton-like reactions on solid catalysts can effectively catalyze the oxidation of organic pollutants at neutral or nearly neutral pH conditions, which is beneficial for *in situ* remediation of polluted groundwater and soils (Matta et al., 2007). In this way, the use of magnetic materials and iron oxide minerals attract more attention, because they are widespread in the natural environment and can be easily applied to *in situ* remediation processes.

Above all, Magnetite (Fe_3O_4) has received much more attention. It is a mixed-valence iron oxide with unique redox properties. Because Fe_3O_4 is a common constituent of soils and sediments, it can be potentially considered as an environmentally benign material for the decontamination of polluted waters and soils (Sun & Lemley, 2011).

Another advantage of magnetic catalyst is that they allow an easy, fast and inexpensive separation upon the application of a magnetic field (magneto-sedimentation) simplifying its recovery and reusability. (Sun et al., 2013). Furthermore, magnetite contains both Fe^{2+} and Fe^{3+} species, which should have a positive effect on the catalytic activity according to Eq. 1 and 2 (Muñoz et al., 2015).

2.5. Zero-Valent Aluminium – acid system

As it has been commented, ZVI has problems with corrosion in presence of oxygen and in addition the accumulation of hydroxide precipitates implies a surface passivation and consequently its loss of metal activity. So it is necessary to study an alternative. System on the base of zero-valent aluminium (ZVAl) seems a promising one. As the main goal is to produce ROS, alternative zero-valent metals with higher efficiency, depends directly on to aspects: the stability of the dissolved metal species against precipitation for wide pH range and the electron transfer of electrons to oxygen. Considering this points, ZVAl is a promising alternative because it can provide a greater thermodynamic driving force for electron transfer compared to ZVI (Bokare & Choi, 2009). The main reason for this enhanced electron transfer is low reduction potential of aluminium ($Al^{3+}/Al = -1.67$ V), meanwhile iron is −0.44V (Fe^{2+}/Fe) (Cheng et al., 2015).

General formation of $HO^{\bullet}$ from hydrogen peroxide in a ZVAl system is described (Eq. 17 and 21). Nevertheless, more intermediate reactions are implied making this process much more complex.

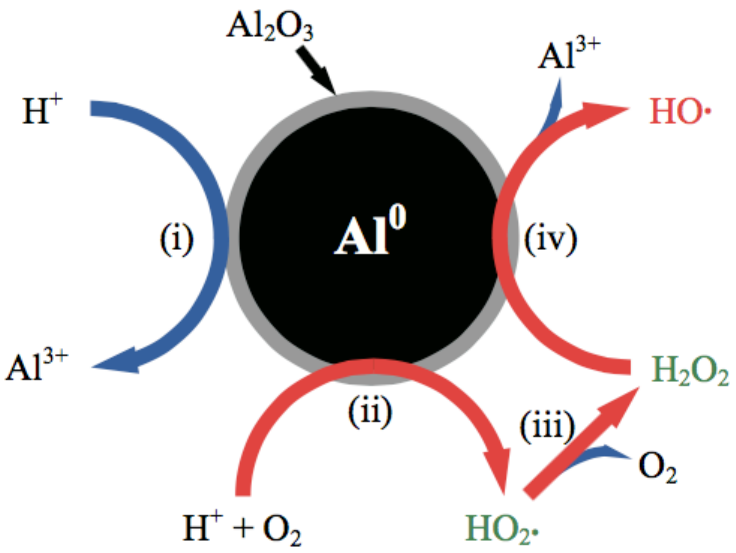

Fig. 1 – Formation of hydroxyl radical in a ZVAl/H^+/air system (Lin et al., 2011)

The first step in the formation of $HO^\bullet$ consists in removing the oxide layer as shown in Fig 1. The commercially available ZVAl has an aluminium oxide (Al_2O_3) layer in the surface. The purpose of this layer is to protect ZVAl of being oxidized and inhibit the activation of oxygen. The second step is the reduction of oxygen under acidic conditions on the aluminium surface forming the radical $HOO^\bullet$ (Eq. 18-19). The rapid disproportion of $HOO^\bullet$ leads to formation of H_2O_2 (Eq. 20). At the end, electron transfer from ZVAl to H_2O_2 generates $HO^\bullet$ (Eq. 22-23). ZVAl is also interesting because it can reduce ferric ions into ferrous ions (Eq. 24).

$$2\ Al^0 + 3\ O_2 + 6\ H^+ \rightarrow 2\ Al^{3+} + 3\ H_2O_2 \quad (17)$$

$$2\ Al^0 + 6\ O_2 \rightarrow 2\ Al^{3+} + 6\ O_2^{\bullet -} \quad (18)$$

$$6\ O_2^{\bullet -} + 6\ H^+ \rightarrow 6\ HOO^\bullet \quad (19)$$

$$6\ HOO^\bullet \rightarrow 3\ H_2O_2 + 3\ O_2 \quad (20)$$

$$Al^0 + 3\ H_2O_2 \rightarrow Al^{3+} + 3\ HO^- + 3\ HO^\bullet \text{ (Fenton-like reaction)} \quad (21)$$

$$Al^0 + 3\ H_2O_2 \rightarrow Al^{3+} + 3\ [H_2O_2]^{\bullet -} \quad (22)$$

$$3\ [H_2O_2]^{\bullet -} \rightarrow 3\ HO^- + 3\ HO^\bullet \quad (23)$$

$$3\ Fe^{3+} + Al^0 \rightarrow 3\ Fe^{2+} + Al^{3+} \quad (24)$$

The presence of Al^{3+} in biological systems can cause the formation of superoxide radical anion.

Superoxide dismutase inhibited only the aluminium-induced effect and not the initial rate of oxidation process in organism. For this reason it is plausible the formation of complex Al^{3+} and superoxide radical anion. Mechanism of formation and chemistry of complex superoxide-aluminium and an explanation for the toxic effects of Al^{3+} in biological systems have been proposed (Hrdlička & Prousek, 2015).

In the present research, Al^{3+} presence is also studied. There is a presumption, that aluminium ions may play a role as a shuttle of electron between Fe^{2+} and H_2O_2 (Eq. 25-26), which leads to hydrogen peroxide decomposition. Al^{2+} ion is known only under extreme condition or it's proposed in different types of complex compounds (Exley, 2012; Kiss, 2013).

$$Fe^{2+} + Al^{3+} \rightarrow Fe^{3+} + [Al^{2+}] \quad (25)$$

$$[Al^{2+}] + H_2O_2 \rightarrow Al^{3+} + [H_2O_2]^{\bullet -} \quad (26)$$

2.6. Chelating Agents

As sludge disposal in classical Fenton process is the main drawback due to iron speciation and precipitation, many chelating agents were employed in order to stabilize the iron in solution at near neutral pH (Sun and Pignatello, 1992).

Regarding heterogeneous Fenton process, it has already overcome the sludge problem by using recyclable catalyst and operating at near neutral pH. Although this process eliminates the sludge disposal problem, there is a reduction in the degradation rates. The addition of chelating agents (CAA) has attracted attention because it seems a viable option to get over Fenton process (homogeneous and heterogeneous) drawbacks.

CAA are chemical compounds (usually organic compounds) that form complexes with metal ions or other substrates. In a homogenous Fenton reaction, the addition of CAA can increase the solubility of Fe^{2+}/Fe^{3+} at neutral pH and the electron transfer and therefore the oxidation rate of organic compounds (He et al., 2015). Regarding heterogeneous Fenton reaction, CAA are able to enhance the oxidation efficiency at near neutral pH by improving the dissolution of iron from the solid surface and then, this dissolved iron can help with $HO^{\bullet}$ generation (Xue et al., 2009).

It has been proved that EDTA is the most effective chelating agent suitable for Fenton type process. In the case of iron-EDTA complex, the effective reduction of Fe^{3+} to Fe^{2+} by hydrogen peroxide drastically improves the iron catalytic power (Pignatello et al., 2006). However, the harmful effects of this chelating agent must be taken into account and their applicability for environmental applications

has been gradually reduced (Al-Abed et al., 2008). Two alternative for EDTA are citric acid (CA) and oxalic acid (OA).

Above all, studies with CA and OA have been focused on improve photo-Fenton process. When UV is applied, it has been found that reactions with OA or CA as a CAA have good results for 2,4-dichlorophenoxyacetic acid mineralization (Lei et al., 2005). Although in the photo-Fenton process citrate shows a lower efficiency than oxalate, citrate is less toxic, is readily available and can be used at higher pH values than oxalate (Silva et al., 2007)

Nonetheless, citrate can adversely affect the effectiveness of Fenton's reaction. CA can inhibit organic compound decomposition by scavenging the $HO^{\bullet}$ and by separating the $HO^{\bullet}$ formation sites from the pollutants (Seol, 2008).

In this research, CA and OA are tested in the presence of Al^{3+} and ZVAl to study its effects on $HO^{\bullet}$ generation rate.

2.7. Influencing factors

Operating pH

Fenton process is strongly dependent on the solution pH due to the iron and hydrogen peroxide speciation conditions. The optimum pH for the Fenton reaction was found to be around 3, regardless of the substrate (Rivas et al., 2001)

The activity of Fenton reagent is reduced at higher pH due to the presence of relatively inactive iron oxohydroxides and formation of ferric hydroxide precipitate. In this situation, less hydroxyl radicals are generated due to the presence of less free iron ions. The oxidation potential of hydroxyl radicals decreases with increasing pH. In addition, auto-decomposition of hydrogen peroxide is accelerated (Eq. 14) at high pH. At pH below 3, decrease in degradation efficiency was observed due to the formation of iron complex species $[Fe(H_2O)_6]^{2+}$ exist, which reacts more slowly with hydrogen peroxide than other species (Babuponnusami & Muthukumar, 2013).

Temperature

Not many studies are available about the effect of temperature on the degradation rate because ambient conditions can be used with good efficiency. Although a study reported that the degradation efficiency is not affected when the temperature is between 10 to 40ºC (Rivas et al., 2001) other research reported that the optimum temperature work is at 30ºC (Lin & Lo, 1997). If the reaction

temperature is expected to rise beyond 40ºC due to exothermic nature, cooling is recommended. The efficient utilization of hydrogen peroxide decreases due to accelerated decomposition of hydrogen peroxide into water and oxygen (Babuponnusami & Muthukumar, 2013).

Ferrous ion concentration

The rate of degradation normally increases with an increase in the concentration of ferrous ion. However, above a certain concentration of ferrous ions, adding more of it, not necessary implies an increase in the degradation rate (Rivas et al., 2001). In addition, an enormous increase in the ferrous ions will lead to an increase in the unutilized quantity of iron salts. These iron salts will contribute to increase the total dissolved solids content of the effluent stream, which is undesired. So, it is very important to perform laboratory scale studies in order to establish the optimum loading of ferrous ions.

Hydrogen peroxide concentration

Concentration of hydrogen peroxide plays an important role to the overall efficiency of the degradation process. It has been usually observed that the efficiency of degradation of the pollutant increases with an increase in the dosage of hydrogen peroxide. However, it is necessary to be careful when selecting the operating oxidant dosage. The unused portion of hydrogen peroxide during the Fenton process contributes to COD value (chemical oxygen demand) and therefore excess amount is not recommended. In addition, the presence of hydrogen peroxide can be harmful to many of the organisms if Fenton oxidation is used as a pre-treatment to biological oxidation. Another negative effect of hydrogen peroxide is the scavenging of generated hydroxyl radicals, which occurs at large quantities of hydrogen peroxide. Thus, as in the ferrous ion concentration, the amount of hydrogen peroxide should be adjusted and based on the laboratory scale studies. (Babuponnusami & Muthukumar, 2013).

3. Materials and Methods

3.1. Chemicals

Monochloroacetic acid ($ClCH_2COOH$, purity >99 %), citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, purity >99 %) and oxalic acid dihydrate ($C_2H_2O_4 \cdot 2\,H_2O$, purity >99 %) were purchased from LACHEMA (Czech Republic). Sulfuric acid (H_2SO_4, purity 96 %) and sodium hydroxide (NaOH, purity >98 %) were purchased from MikroCHEM (Slovakia). As a source of ZVAl (Al^0) aluminium foil (99.5 % purity) was used and before reaction was activated by NaOH (conc. 5 %), and rinsed three times with deionized water. The chemicals for the chloride ions determination were: potassium dichromate ($K_2Cr_2O_7$, purity >99.8 %) purchased from LACHEMA (Czech Republic), silver nitrate ($AgNO_3$, Purity >99.5 %) was purchased from LPChem (Slovakia).

3.2. Equipment

For mixing during reaction time Stirrer Heidolph MR Standard was used. Adjusted initial and final pH´s were determined by pH-meter HANNA Instruments HI2002-02 with HI1131B probe. UV spectrum of each final sample was measured in the spectrophotometer HACH LANGE HQ30D with LDO10101 probe

3.3. Experiments

The procedure used in all experiments was: pH of MCA solution ($5 \cdot 10^{-3}$ M) was adjusted by H_2SO_4 solution (conc. 5%) to pH 3 ± 0.1. Into different 250 mL Erlenmeyer 100 mL of MCA solution and 0.1 g of $FeSO_4 \cdot 7H_2O$ (M = 278.0 $g \cdot mol^{-1}$) was added. Depending on the set of experiments, an amount of $Al_2(SO_4)_3 \cdot 18H_2O$ (M = 666.0 $g \cdot mol^{-1}$) or ZVAl previously activated with NaOH (5 %) and subsequently washed by deionized water were added. In addition, chelating agents such as oxalic acid dihydrate (M = 126.1 $g \cdot mol^{-1}$) or citric acid monohydrate (M = 210.1 $g \cdot mol^{-1}$) were added depending on the experiments.

Afterwards, 0.1, 0.2, 0.4, 0.8 mL of H_2O_2 (conc. 5%) were added depending on reaction condition. Flasks were covered with aluminium foil due to the photosensibility of the reaction.

3.4. Analysis

After 30, 60, 120, and 180 minutes 10 mL of sample was taken. Samples were neutralized by NaOH (conc. 5 %), filtrated and diluted in 100 mL flasks. At last, all the samples were titrated using $AgNO_3$ ($5 \cdot 10^{-3}$ M) and $K_2Cr_2O_7$ (5 %) as indicator according Horáková (2012).

The UV spectrum of each final sample (after 180 min) was measured in the spectrophotometer between 190 and 400 nm.

3.5. Toxicity tests

Toxicity tests were performed on the terrestrial plant seeds *Sinapis Alba* (Mustard) according to OECD Guidelines 208: "Terrestrial plants, Growth tests" method. *Sinapis Alba* seeds were purchased from Forestina (Czech Republic). All seeds were visually inspected and undamaged seeds with similar size were used in experiment. All experiment tests were carried out in Petri dishes with diameter of 10 cm, which were lined with filter paper. To every Petri dish were added 30 seeds in geometric configuration. All solutions were adjusted to pH 7.0 and after dilution with dilution water in ratio 1:1, 5 mL of sample was added into Petri dishes. Used experimental conditions were as follows: Exposure time was 72 hours, experimental temperature was 20 ± 1°C, and all tests were carried out in the dark under air-equilibrated conditions in three parallels. As reference sample deionized water diluted by dilution water was used. Next test was carried out with standard DCF solutions. Finally, solutions obtained after treatment processes with ZVAl/H+ system and with Al^{3+} ions at the initial pH of 3.0 were also tested. Subsequently statistical evaluation of the growth inhibition of *Sinapis Alba* roots was done in all experiments.

4. Results and discussion

In the following sections results are presented. It is important to remember that all the experiments performed had the same amount of iron ions.

4.1. Classical Fenton Reaction

As is shown in Fig. 2, classical Fenton reaction (FR) has in our mild conditioned experiments only 3 % efficiency (addition of 0.1 mL of H_2O_2). With higher amount of added H_2O_2 the efficiencies increased. In experiment with the highest amount of added H_2O_2 (0.8 mL) degradation efficiency achieved 36 %. FR reaction produces $HO^{\bullet}$ radicals, which immediately react with MCA and starts its oxidative degradation (Eq. 26, 27). Known products of MCA oxidative degradation are formic and oxalic acid (Hrdlička, 2014).

$$HO^{\bullet} + ClCH_2COOH \rightarrow H_2O + ClC^{\bullet}HCOOH \quad (26)$$

$$ClC^{\bullet}HCOOH + O_2 \rightarrow\rightarrow \text{Products of oxidative degradation} \quad (27)$$

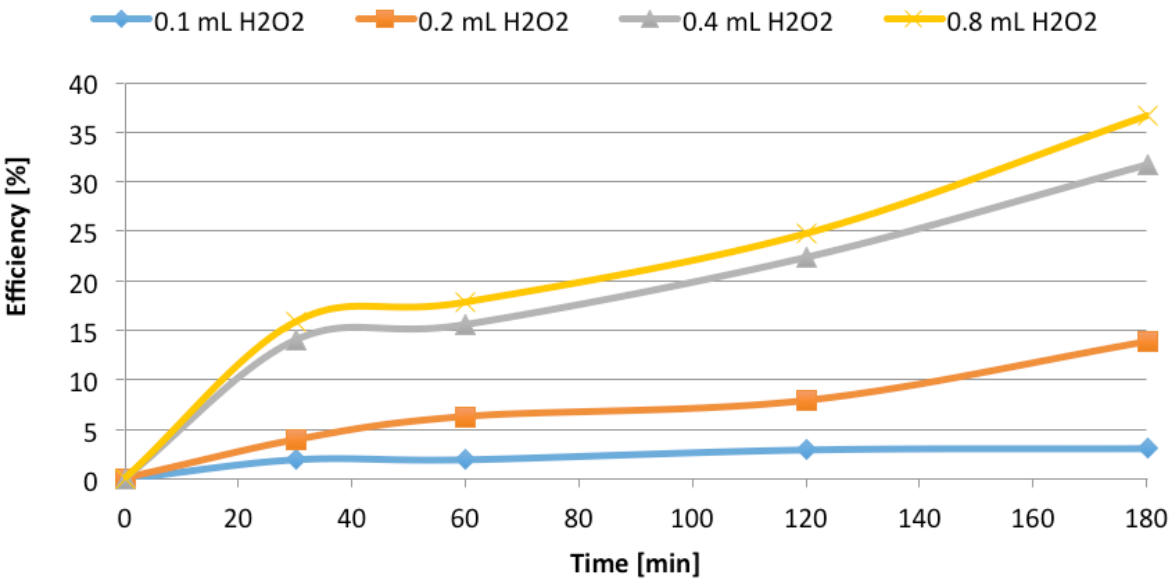

Fig.2: Efficiency of MCA degradation in classical Fenton reaction with initial $pH_i = 3.0 \pm 0.1$ for different amounts of H_2O_2 and for different reaction times.

4.2. ZVAl and Al^{3+} ions

As shown in Fig. 3, with addition of 0.1 mL of H_2O_2 the best results were achieved with addition of Al^{3+} (molar ratio Fe^{2+}/Al^{3+} 1:5), with an efficiency of 23.6 %. In the other hand, an efficiency of 17.8 % was achieved with the addition of 0.2 g of ZVAl. In these two experiments, it seems that after 3 hours the reaction is still running.

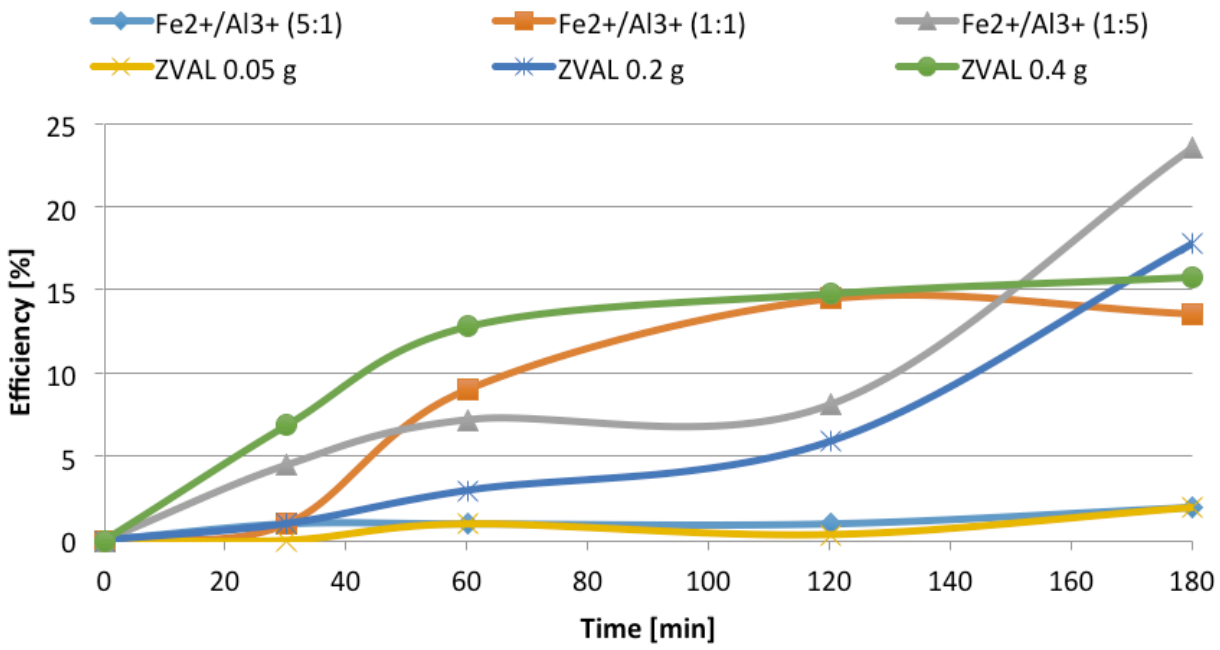

Fig.3: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pH_i = 3.0 ± 0.1 for 0.1 mL of H_2O_2 and for different reaction times.

Unless those experiments with the fewest amount of Al^{3+} or ZVAl, the efficiency was increased if it is compared with FR with 0.1 mL of H_2O_2. From obtained results it is clear that ZVAl and Al^{3+} ions in small amount have no effect to reaction rate.

When 0.2 mL of H_2O_2 have been added, a stoichiometric amount of Al^{3+} has the highest efficiency (27.3 %) as can be seen in Fig. 4, which is almost two times higher than in the case of addition of 0.1 mL H_2O_2. Regarding ZVAl, all samples are between 20-23 % of efficiency after 3 hours of reaction. In these experiments, the biggest part of the degradation is achieved after 1 hour of reaction. After that, the reaction rate is decreased or it is even null depending on the samples. In all systems with addition of ZVAl was achieved improvement of classical FR in the range from 28 to 64 %.

Again, only with the fewest amount of Al^{3+} the efficiency is not increased if compared with FR.

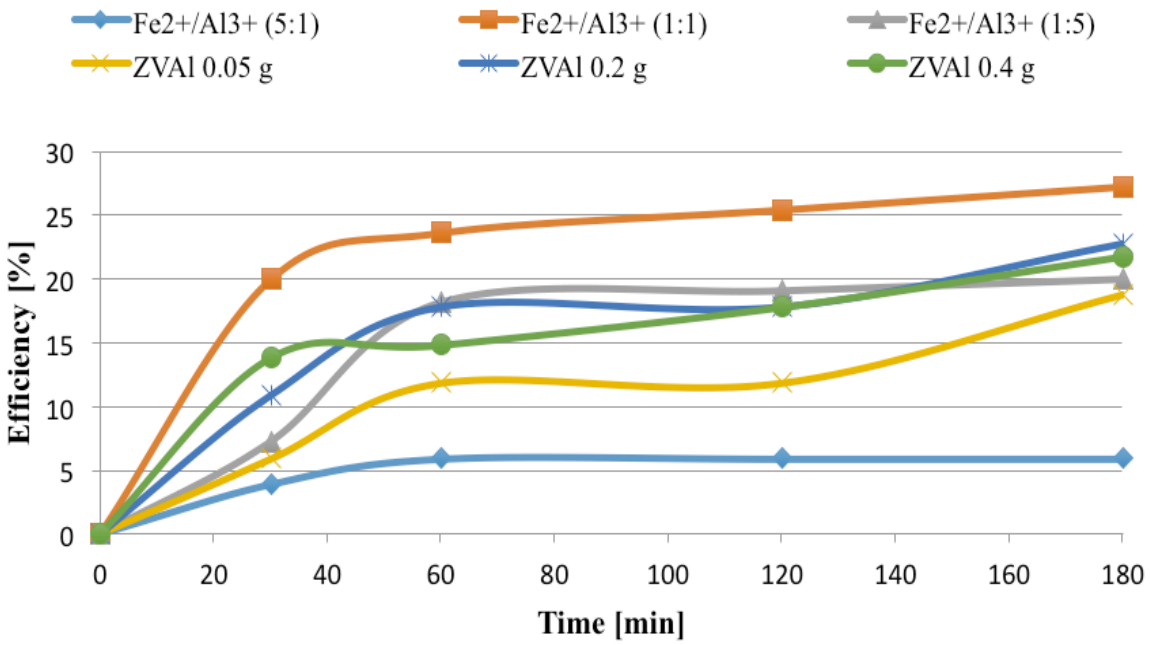

Fig.4: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pH_i = 3.0 ± 0.1 for 0.2 mL of H_2O_2 and for different reaction times.

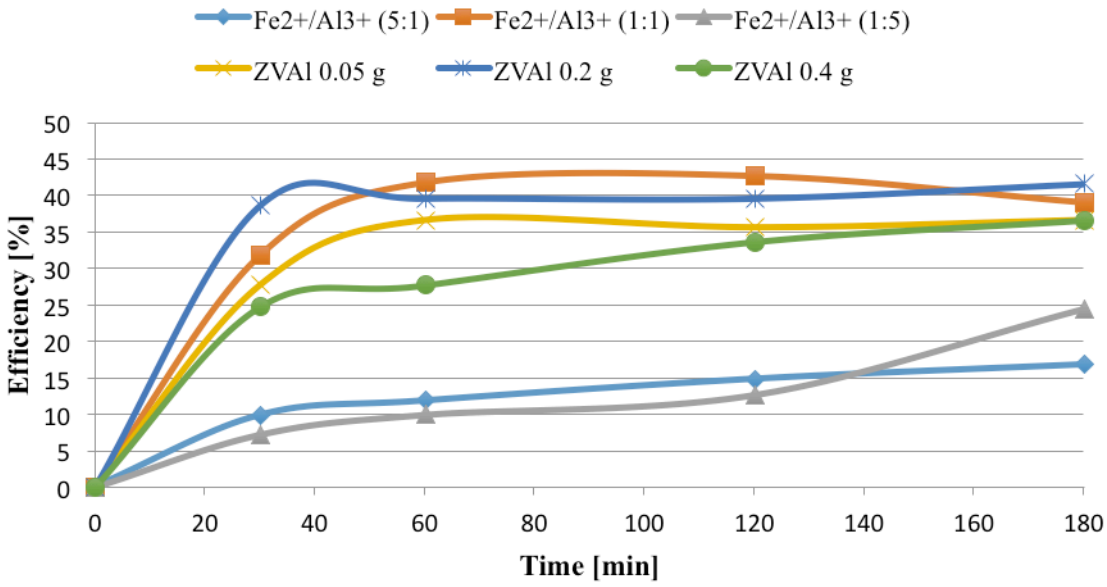

Fig.5: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pH_i = 3.0 ± 0.1 for 0.4 mL of H_2O_2 and for different reaction times.

The Fig. 5 shows the results when 0.4 mL of H_2O_2 was added. In the case of Al^{3+}, again, only the stoichiometric amount shows the best efficiency (39 %) than in classical FR (31 %) for the same amount of H_2O_2. Lower and higher amount inhibit the reaction. Cause of this observed inhibition may be the scavenging effect of Al^{3+} in single electron transfer.

Regarding ZVAl, all amounts show higher efficiency than in FR. The efficiency from lower to higher amount of ZVAl is 36.5, 41.6 and 35.7 % which is 1.5, 1.31, 1,12 times higher than in the case of FR. Once again, the improvement of FR was achieved and reaction rate was stopped after 1 hour because of all H_2O_2 in reaction mixture was consumed.

Finally, the results for the highest amount of H_2O_2 (0.8 mL) are presented in Fig.6. In this case, all the ZVAl experiments show a higher efficiency, which reaches 63 % when 0.4 g of ZVAl was added. Compared to FR this is 1.75 times higher. The explanation for the better results of ZVAl is due to the fact that ZVAl can reduce ferric ions into ferrous ions (Eq. 24) and they can react again with H_2O_2, which is in this case in the highest dose.

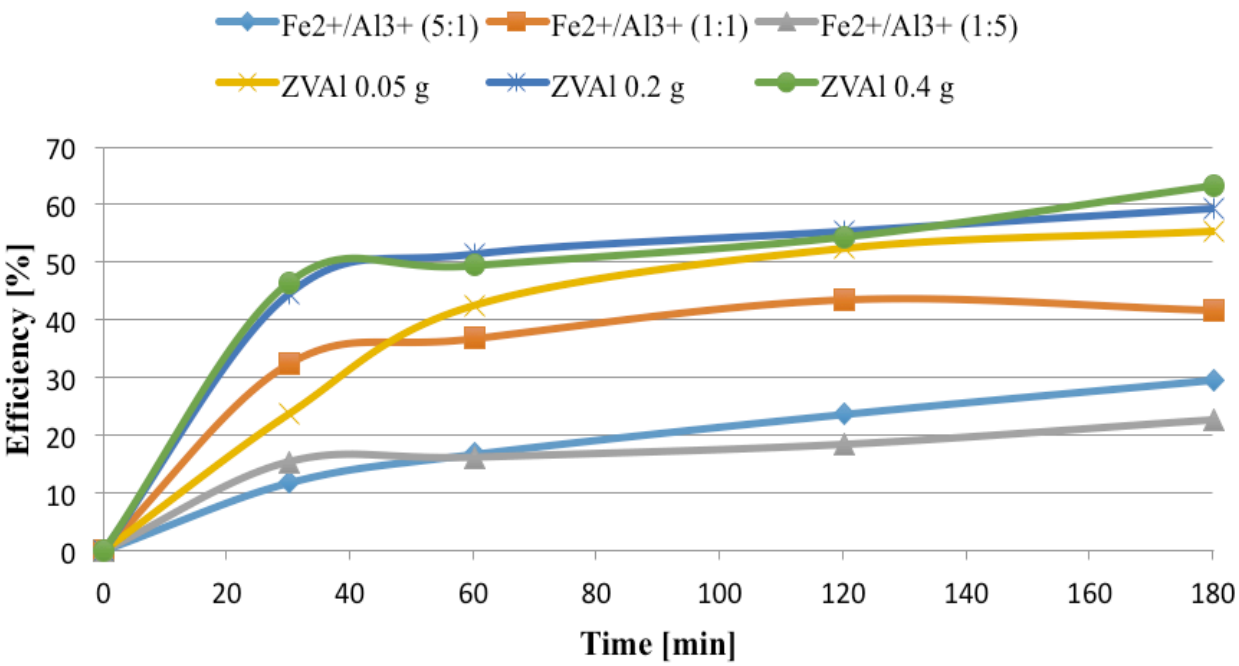

Fig.6: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pH_i = 3.0 ± 0.1 for 0.8 mL of H_2O_2 and for different reaction times.

For the samples with Al^{3+}, again, only the stoichiometric amount improves FR (42 % to 36 %). Lower and higher amounts seem to inhibit the reaction for the same reasons explained above.

Some experiments without ferrous ions have also been performed to study the Eq. 17. However, no efficiency has been observed after 3 hours of reaction. It seems that the explanation is the kinetic constant, which is very low. Probably, with longer duration of experiments, some efficiency would be observed.

Anyway, there is a non-linear dependence between the amount of H_2O_2 used and the obtained efficiency. This fact means that there is no easy to say which of the H_2O_2 amount is better. As seen in the results, it is possible to reach high efficiency of degradation but it always implies more cost of reagents.

In addition experiments with 30 % H_2O_2 and addition of Al^{3+} (molar ratio Fe^{2+}/Al^{3+} 5:1) and ZVAl (0.2 g) were performed. The results show that in the case of experiments with addition of 0.8 mL of H_2O_2 efficiency achieved 72 and 90 %, respectively. All H_2O_2 was consumed in two hours of reaction (Fig. 7). These experiments confirmed our prediction that no H_2O_2 left in the case of reaction with addition of 5 % H_2O_2 after 1 hour.

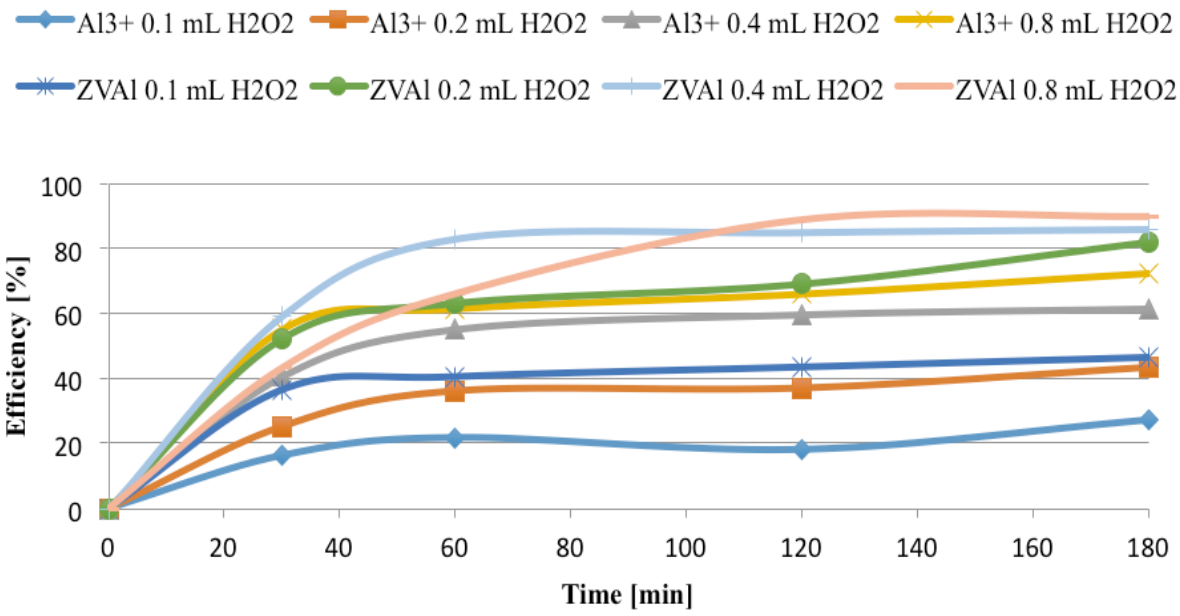

Fig.7: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pH_i = 3.0 ± 0.1 for 5:1 molar ratio Fe^{3+}/Al^{3+} and 0.2 g of ZVAL and for different reaction times with the addition of 30 % H_2O_2.

4.3. Chelating agents effect

The results for OA and CA are presented. The efficiency after 180 min is given for all the experiments and only for those with improved efficiency the evolution over time is presented.

4.3.1. Oxalic Acid

The results of experiments performed with OA and Al^{3+} are presented in Fig. 8. For a ratio of Fe^{2+}/Al^{3+} 5:1 and 0.4 mL of H_2O_2 the efficiency is higher with addition of OA in amount of 1, 5 and 10 mg than without OA (23 %, 30 % and 22 % instead 17 %). However, the efficiency is still lower than in classical Fenton reaction (32 %). With the addition of 0.8 mL of H_2O_2 the efficiency is also higher than without OA (32 %, 35 %, 38 % for 30 % without), but again, this is not enough to improve classical Fenton reaction (38 %).

For a ratio of 1:1 and an addition of 0.4 mL an inhibition of the reaction is observed. In other hand when 0.8 mL were added and for 5 mg of OA the efficiency reaches 41 % which is bit better than without OA (40 %) and in classical Fenton reaction (38 %).

Finally, when the ratio is 1:5, there is a clear pattern that with more OA the efficiency is better. Although this fact, the efficiency is still lower than in classical Fenton reaction for all the samples.

From these results is possible to say that OA play the role of scavenger in all performed experiments and combination of OA and addition of Al^{3+} hasn't enhanced effect to FR.

The results for experiments with ZVAl are shown in Fig. 9. For the lowest amount of ZVAl the results for 0.4 mL and for 0.8 mL of H_2O_2 are very similar among them, which indicate that OA may not be influencing the reaction. In fact, the efficiency for these experiments without OA is 37 % and 56 % for each amount of H_2O_2. This is a very similar efficiency when OA is added as it is seen in Fig. 9.

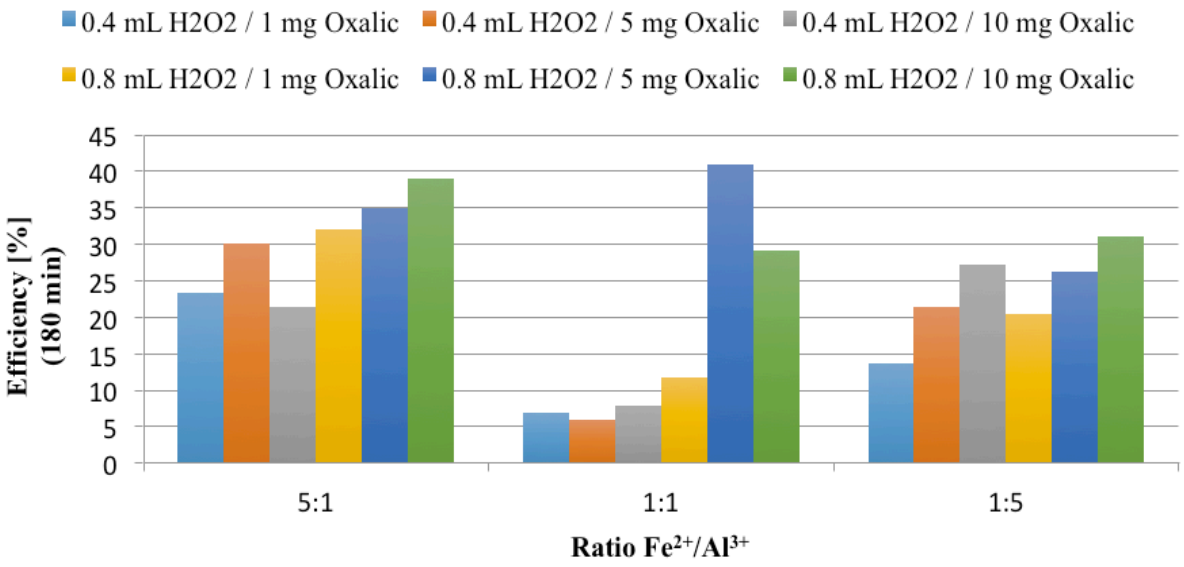

Fig.8: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pH_i = 3.0 ± 0.1 and different amounts of reagents after 3 hours.

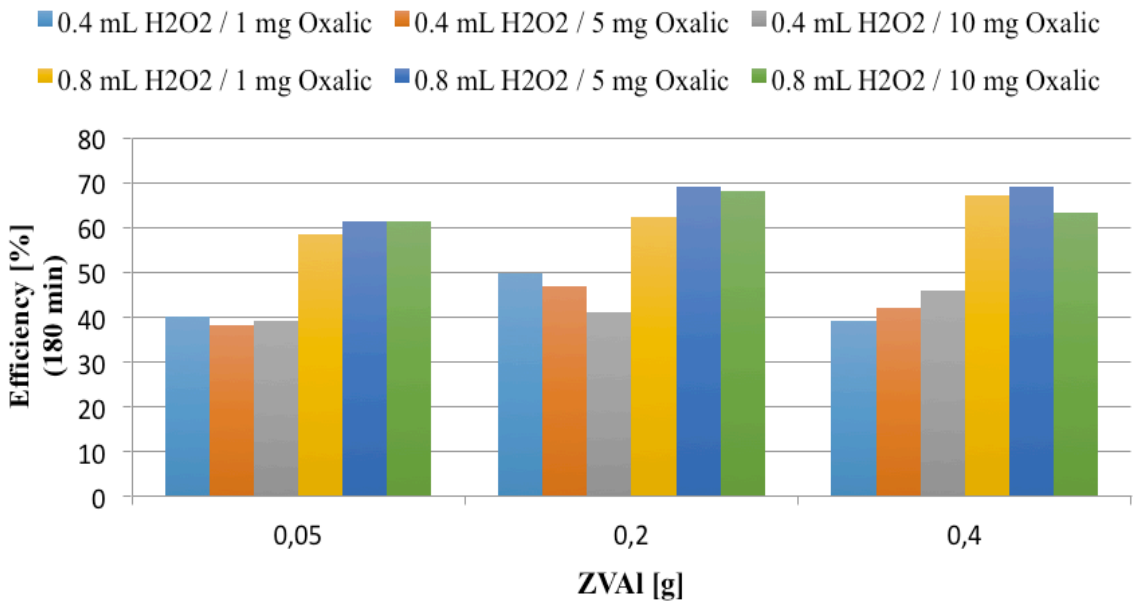

Fig.9: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pH_i = 3.0 ± 0.1 and different amounts of reagents after 3 hours.

For 0.2 g of ZVAl the efficiency was increased with OA. When 0.4 mL of H_2O_2 are added, higher efficiency is achieved with 1 mg of oxalic (50 %). With 5 mg and 10 mg of OA the efficiency is 47 % and 41 % which is higher than the reaction without OA (41 %). With the addition of 0.8 mL of H_2O_2 60 % efficiency (experiment without oxalic acid) is exceeded for all amounts of OA, being with 5 mg the maximum (69 %).

Finally, with 0.4 g of ZVAl all samples with OA overtake those experiments without it. For 0.4 mL of H_2O_2 37 % is the efficiency without OA, which has been improved until 43 % with 10 mg of OA. In the case of 0.8 mL, 63 % is the efficiency without OA. With the addition of 5 mg of OA the efficiency reaches 69 %.

Some experiments with OA and without Al^{3+} and ZVAl have been also performed. In all these cases the efficiency is lower than when Al^{3+} and ZVAl were added. In generally, we can suggest that OA in the case of systems with ZVAl cause better transfer of electron from ZVAl surface to in FR produced Fe^{3+} ions or to H_2O_2. However, this effect had only small influence for observed degradation efficiency.

4.3.2. Citric Acid

In contrast to OA, CA had higher degradation efficiency than OA in all experiments when it was combined with Al^{3+}.

As shown in Fig. 10, when 0.4 mL of H_2O_2 was added and for the lowest amount of Al^{3+} the efficiency reached 26 % at its maximum which is lower than classical Fenton reaction (32 %). In this case the results are very similar with OA. When 0.8 mL of H_2O_2 was added and for a ratio Fe^{2+}/Al^{3+} of 5:1, the efficiency clearly gets over the classical Fenton reaction (36 %) reaching 45 % and 41 % with 5 and 10 mg of CA, respectively.

Regarding stoichiometric ratio Fe^{2+}/Al^{3+}, with the addition of 0.4 mL of H_2O_2 the efficiency gets over classical Fenton (32 %) only combined with 10 mg of CA, until 50 %. On the other hand, when 0.8 mL was added, both 5 and 10 mg of CA show higher efficiency than in classical Fenton reaction (42 % and 50 % / 36 % FR).

When the ratio is 1:5, all samples get over classical Fenton efficiency (32 % for 0.4 mL and 36 % for 0.8 mL of H_2O_2). Higher efficiency is achieved with 5 mg of citric in the case of 0.4 mL of H_2O_2 (43 %). When 0.8 mL of H_2O_2 was added, the efficiency reached 48 % with 1 mg of CA.

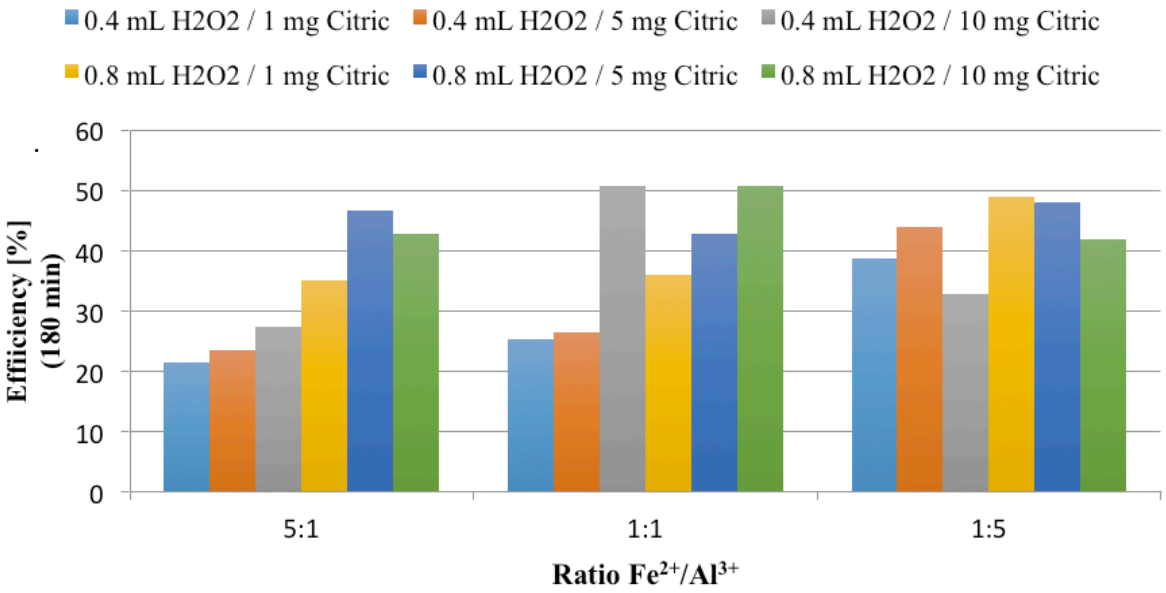

Fig.10: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pHi = 3.0 ± 0.1 and different amounts of reagents after 3 hours.

On the other hand, the addition of CA combined with ZVAl gets over classical Fenton reaction efficiencies in all the experiments performed so, it is a better option to compare it with the reaction without adding citric acid (Fig. 11).

With the lowest amount of ZVAl, only with 1 mg of CA the efficiency is higher than reaction without CA when 4 mL of H_2O_2 were added. With the addition of 0.8 mL of H_2O_2 all samples get over the efficiency of experiments without CA (55 %) being 63 % it's maximum.

In the case of 0.2 g of ZVAl and 0.4 mL of H_2O_2 there is not a clear efficiency improvement compared with efficiency without CA. However, when 0.8 mL of H_2O_2 was added, the efficiency reaches 76 % with 5 mg of CA, which is the highest efficiency in the whole study.

Finally, with the maximum amount of ZVAl and with the addition of 0.4 mL of H_2O_2 only with 10 mg of CA the efficiency of 59 % gets over the efficiency of the same reaction but without citric acid (37 %). When 0.8 mL of H_2O_2 were added, the efficiency is 70 %, 74 % and 56 % for 1, 5 and 10 mg of CA. The same reaction without CA has an efficiency of 63 %.

Some experiments with CA and without Al^{3+} and ZVAl have been also performed. In all these cases the efficiency is lower than when Al^{3+} and ZVAl are added.

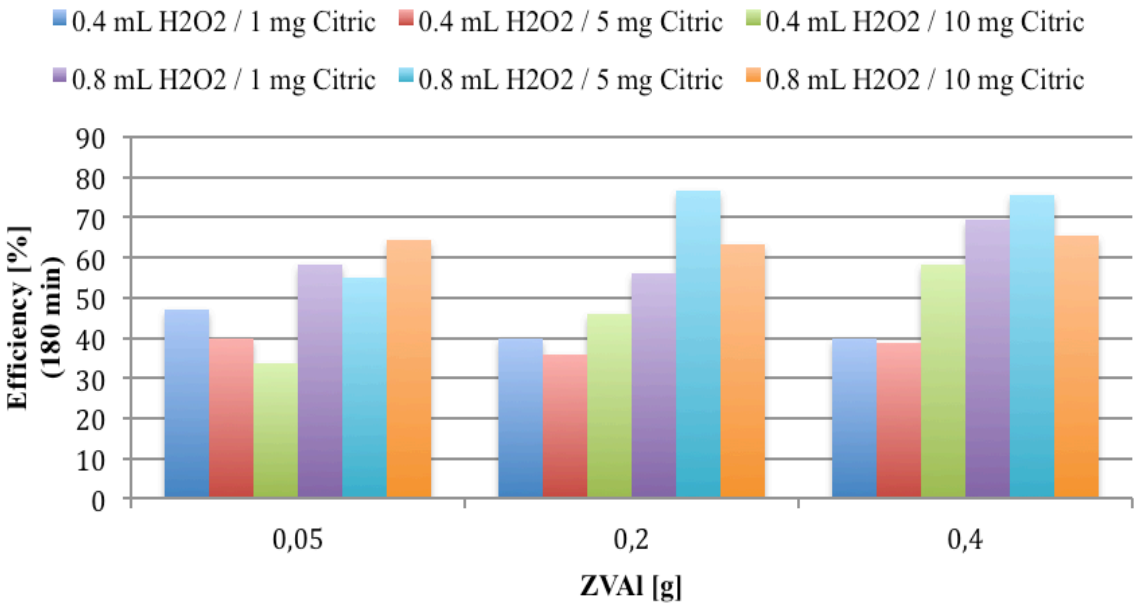

Fig.11: Efficiency of MCA degradation in aluminium modified Fenton reaction with initial pHi = 3.0 ± 0.1 and different amounts of reagents after 3 hours.

5. Environmental impact: Toxicity tests

Toxicity test of CA and OA have been performed as well as for the samples of the experiments with best efficiency. As it can be seen in Fig. 12 the toxicity test for OA shows no clear difference about the inhibition between the different concentrations. Also, from the germination rate it is no possible to conclude any significance evidence.

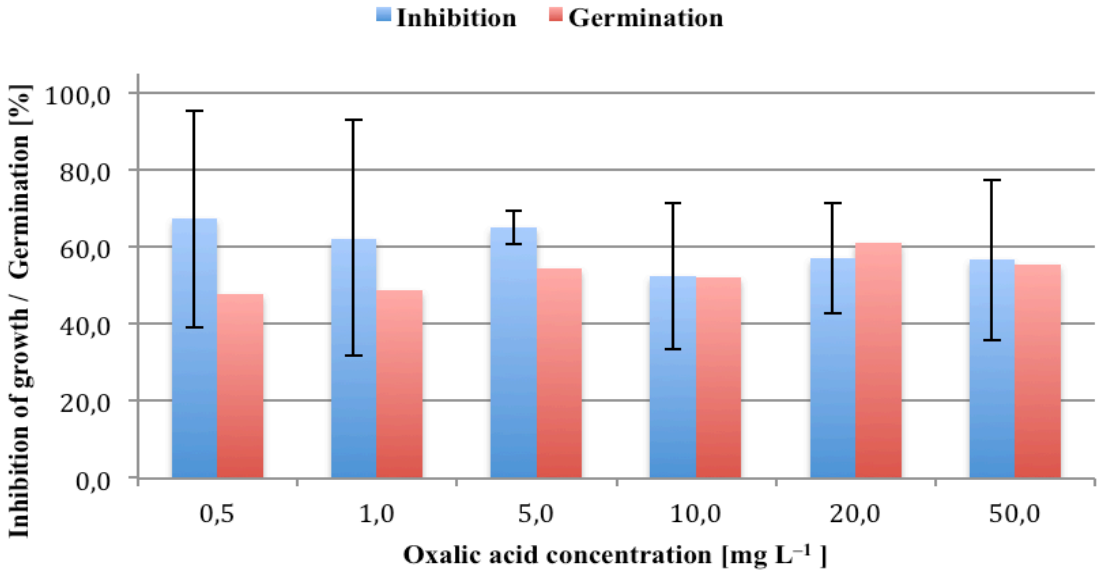

Fig.12: Inhibition of growth and germination of *Sinapis Alba* seeds by oxalic acid solutions in concentration from 0.5 to 50 mg L^{-1}.

In the other hand Fig. 13 shows the inhibition and germination for CA. Once again, all the results are very similar and there is no evidence that raising or decreasing the amount of CA has an effect on the seeds.

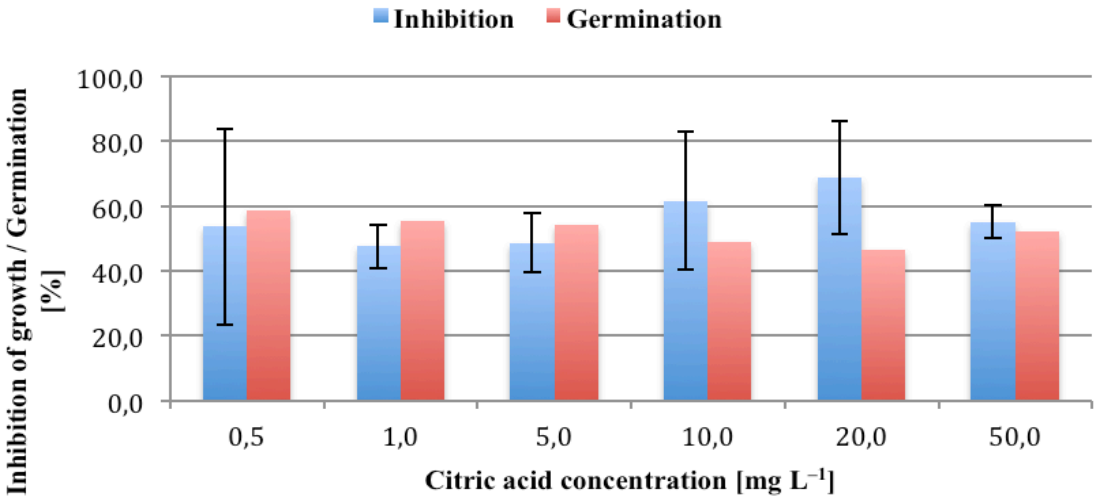

Fig.13: Inhibition of growth and germination of *Sinapis Alba* seeds by citric acid solutions in concentration from 0.5 to 50 mg L^{-1}.

Fig.

14 shows the inhibition and germination for different samples after 3 hours of reaction. Conditions of each experiment can be found in table 7. For the experiments 3,5 and 7 the inhibition is very low or even the samples positively affect the growth of the seeds so it is possible to say that ZVAl is good alternative to treat MCA because of its high efficiency and because of the low toxicity of its final products.

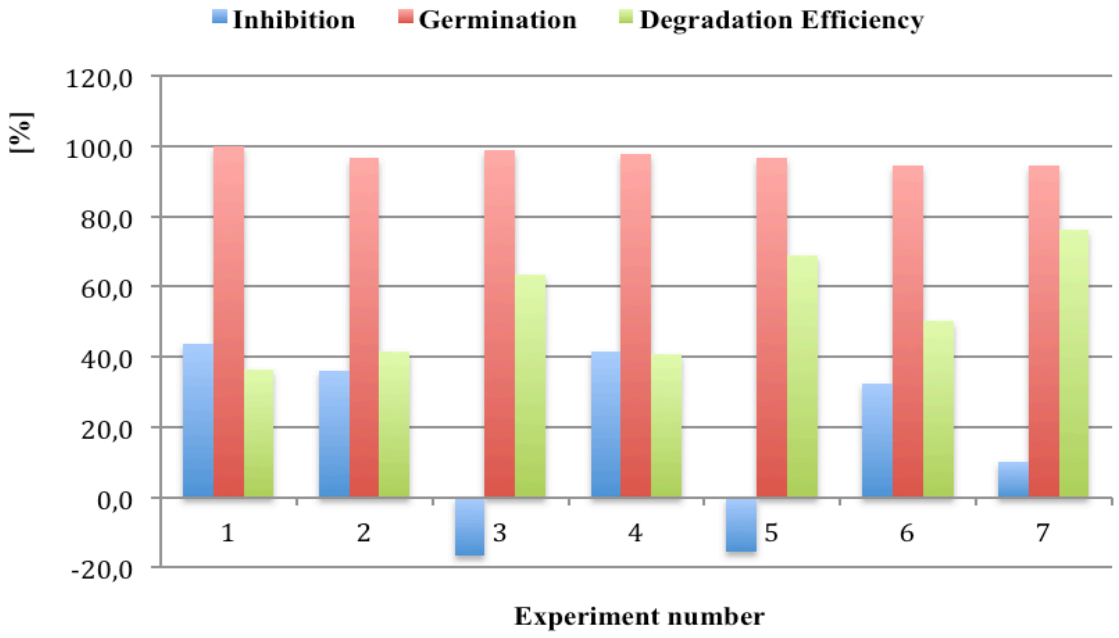

Fig.14: Inhibition of growth and germination of *Sinapis Alba* seeds of different experiments after 3 hours of reaction. The efficiency of each experiment is also showed.

In the case of Al^{3+}, there is no difference about final products toxicity compared with classical Fenton reaction. In addition, there is also no clear difference between the toxicity effect of OA and CA as commented previously.

6. Kinetic constants

Kinetic constants for experiments with highest efficiency (for each composition of reagents) have been calculated and can be seen in table 7. After seeing the concentration of pollutant over time it was expected that the reaction follow a second order kinetic. The correlation coefficient corroborates this hypothesis. All the kinetics constants calculated belong to a reaction with the same amount of iron ions and H_2O_2 (0.8 mL).

Table 7 – Second order kinetic constants for experiments with highest efficiency and its increase over classical Fenton reaction

Experiment	k_2 (L mg^{-1} min^{-1})	R^2	Variation
Classical Fenton	0.0080	0.9686	Standard
Fe^{2+}/Al^{3+} (1:1)	0.0020	0.8576	2.61
ZVAl 0.4 g	0.0055	0.9360	7.12
Fe^{2+}/Al^{3+} (1:1) + 5 mg OA	0.0012	0.9519	1.54
ZVAl 0.4 g + 5 mg OA	0.0142	0.9486	18.38
Fe^{2+}/Al^{3+} (1:1) + 10 mg CA	0.0020	0.9552	2.65
ZVAL 0.2 g + 5 mg CA	0.0125	0.9876	16.16

As it is shown in table 7, the highest reaction rate is with 0.4 g of ZVAl and 5 mg of OA, which is 18.38 times higher than for the classical Fenton reaction. In addition, when 0.2 g of ZVAl and 5 mg of CA were added the reaction rate is also much higher (16.16 times) than in classical Fenton reaction. On the other hand, kinetic constant with Al^{3+} is increased but in a less prominent way. In all the experiments, the reaction rate is increased between 1.5 and 2.6 times than in classical Fenton reaction.

It seems clear that ZVAl can enhance reaction rate much more than Al^{3+}.

7. Conclusions

Classical Fenton reaction has been successfully modified with the addition of Al^{3+} and ZVAl and all the experiments performed in this study have been able to degrade MCA.

In the case of Al^{3+} it has been observed that only when a stoichiometric amount is added in relation with iron, the degradation efficiency is enhanced for all the different amounts of H_2O_2. There is the presumption that with fewer and higher amounts, Al^{3+} can play a role as a scavenger in the single electron transfer.

Regarding ZVAl, it has shown great improvement of the classical Fenton reaction. Efficiency of 63% has been achieved probably because ZVAl has the ability to reduce ferric ions into ferrous ions, so it acts as a catalyst regenerator.

OA seems to inhibit the reaction because there is no significant improvement when small amounts were added. On the other hand, CA has been able to enhance the degradation. The combination 0.2 g of ZVAl and 5 mg of CA has reached 76 % of efficiency, which is the maximum achieved among all the experiments.

Toxicity tests show no clear difference between CA and OA. Both of them inhibit the seeds in the same proportion. In the other hand, ZVAl seems the best alternative due to its high degradation efficiency. That fact make the final product of reaction less toxic and even can stimulate the growth of the seeds.

Kinetic constant of the best reactions have been calculated. They confirmed that the degradation of MCA with aluminium modified Fenton process is a second order reaction and the reaction rate has been improved 18.38 times over classical Fenton reaction.

8. References

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